

The Dissociation of Electrolytes in
Nonaqueous Solvents as Deter-
mined by the Conductivity and
Boiling-Point Methods

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

HENRY ROYER KREIDER

June, 1910

EASTON, PA.
ESCHENBACH PRINTING COMPANY
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This investigation was undertaken at the suggestion of Professor Jones and pursued under his direction.

The Dissociation of Electrolytes in Nonaqueous Solvents as Determined by the Conductivity and Boiling-point Methods

Four methods have been devised for measuring the dissociation of salts in solution: The conductivity and freezing-point methods, the solubility method of Nernst and Noyes, and the boiling-point method. Of these the conductivity and freezing-point methods are the best known, and are the most accurate. The solubility method of Nernst and Noyes is not widely applicable. Within recent years the boiling-point method has been so much improved by Jones and others that it gives fairly accurate results.

There are certain objections to all of these methods. The conductivity and the freezing-point methods give good results in aqueous solutions, but in nonaqueous solutions which are less dissociated, their use has been attended with difficulty. In many of these solvents it has not been possible, previous to the present time, to determine μ_{∞} accurately, and, consequently, the dissociation could not be calculated from the results obtained by the conductivity method. Many of the nonaqueous solvents freeze at a temperature so far below the ordinary that the application of the freezing-point method is often impossible.

By means of the latest type of cell devised in this laboratory, and which will be described later, we have been able to measure μ_{∞} for a number of salts in methyl and ethyl alcohols, and thus to calculate the dissociation of these salts in these solvents from the data obtained by the conductivity method. The dissociation of these same salts in the same solvents was determined by the boiling-point method with the object of finding if any relation exists between the results obtained by the two methods.

HISTORICAL REVIEW.

A large amount of work has been done with nonaqueous

solvents, especially with the lower alcohols of the aliphatic series. These were soon found to have the property of dissociating salts to a considerable extent. Fitzpatrick¹ studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride and calcium chloride in both methyl and ethyl alcohols, and found values which were considerable, though less than those in water. Hartwig² measured the conductivity of a number of organic acids in both methyl and ethyl alcohols. Paschow³ worked with potassium iodide, cadmium iodide, calcium iodide, potassium acetate and sodium acetate in methyl alcohol. Vicentini⁴ measured the conductivities of a number of salts of these alcohols. Cattaneo,⁵ working with salts in ethyl alcohol, found that a number of those with which he worked have a negative temperature coefficient in this solvent. Vollmer⁶ studied several salts over a large range of dilutions. Holland⁷ investigated the effects of non-electrolytes on the conductivity of various salts in methyl alcohol. Carrara's⁸ work is very important. He carried out an extensive investigation on a large number of salts in methyl alcohol. Walden⁹ did a large amount of work with pure organic solvents. The work of Dutoit and Aston¹⁰ and of Frederich¹¹ is important. They formulated the hypothesis that the dissociating power of a solvent is a direct function of its degree of association in the pure state. Other workers in this field are Kablukoff,¹² Vollmer,¹³ and Kahlenberg and Lincoln.¹⁴

Mixed Solvents.

Wakeman¹⁵ carried out an investigation on organic acids in

¹ Phil. Mag., **24**, 378 (1893).

² Wied. Ann., **33**, 58 (1888); **43**, 838 (1891).

³ Charcow, 1892.

⁴ Beibl., Wied. Ann., **9**, 131 (1885).

⁵ *Ibid.*, **18**, 219, 365 (1894).

⁶ Wied. Ann., **52**, 328 (1894).

⁷ *Ibid.*, **50**, 263 (1893).

⁸ Gazz. Chim. Ital., [1] **26**, 119 (1896).

⁹ Z. physik. Chem., **5**, 35 (1890).

¹⁰ Compt. rend., **125** 240 (1897).

¹¹ Bull. Soc. Chim., [3] **19**, 321 (1897).

¹² Z. physik. Chem., **4**, 432 (1889).

¹³ Wied. Ann., **52**, 328 (1894).

¹⁴ J. Phys. Chem., **3**, 26 (1899).

¹⁵ Z. physik. Chem., **11**, 49 (1893).

mixtures of water and ethyl alcohol and found that the conductivity of these substances in these solutions decreased with increasing amounts of alcohol. Zelinski and Krapiwinski¹ point out that the salts with which they worked, the iodides and bromides of sodium and ammonium in mixtures of 50 per cent. methyl alcohol and water, give a conductivity considerably less than the conductivity of these salts in either pure alcohol or water. Cohen² gives similar results with ethyl alcohol and water, and finds that potassium iodide in 80 per cent. alcohol shows a larger conductivity below $V = 512$ than in pure alcohol, but at a greater dilution the conductivity is less in the mixed solvents than it is in either of the pure solvents. Wakeman,³ working with mixtures of ethyl alcohol and water, found that the equation,

$$\frac{\Delta}{p(100-p)} = \text{constant}$$

held for many substances in mixtures of the above-named solvents (Δ is the difference between the conductivity of the electrolyte in water and in the mixture, and p the percentage of alcohol by volume).

From his own and from Wakeman's observations Cohen points out the following relation:

$$\frac{\mu_v \text{H}_2\text{O}}{\mu_v \text{H}_2\text{O.Alc.}} = \text{constant.}$$

This relation holds independently of temperature and concentration. He remarks that either the dissociation of the salt with which he worked is the same or that in these mixtures conductivity is not a direct measure of dissociation. Roth later found that the relation given by Wakeman holds, while that given by Cohen does not.

Jones⁴ and his coworkers have done a fairly large amount of work on conductivity and viscosity in mixed solvents. Since the following is essentially a continuation of that work a very brief review of the latter is necessary.

¹ Z. physik. Chem., **21**, 35 (1896).

² *Ibid.*, **25**, 31 (1898).

³ *Ibid.*, **11**, 49 (1893).

⁴ Publication No. **80**, Carnegie Institute.

Jones and Lindsay¹ found that the phenomenon discovered by Zelinski and Krapivin is not confined to a few salts in mixtures of methyl alcohol and water only, but that it holds over a large range of salts and also in ethyl alcohol-water mixtures. It holds less generally at 25° than at 0°, and in ethyl alcohol-water mixtures less than in methyl alcohol-water mixtures. The conductivities were always less than the mean calculated from the conductivities in the pure solvents.

As a partial explanation they advance the following tentative suggestion: According to the theory of Dutoit and Aston only the polymerized molecules of the solvent dissociate the molecules of the solute. It is well known that water and the alcohols used are highly associated substances. On coming into contact with each other, they break down the association of each other until equilibrium is reached; and, consequently, they have less dissociating power. In methyl alcohol-water mixtures where association of the constituents is greatest the dissociation is greatest. Other facts are in accordance with this suggestion. Since at the lower temperatures the association is greatest in the constituents, we would expect the greatest abnormality here. And such is the case.

These conclusions were subsequently further confirmed by the cryoscopic work of Jones and Murray.² They worked with water and formic and acetic acids, and determined the molecular weights of each in the other by the freezing-point method. They found that the molecular weights of these substances are always less than the molecular weights of the pure substances as determined by the method of Ramsay and Shields. They thus conclude that the action of an associated solvent upon another associated solvent is analogous to the action of an associated solvent upon an electrolyte.

Jones and Carroll³ extended the work of Jones and Lindsay. They worked with both binary and ternary electrolytes. As solvents they used methyl and ethyl alcohols and mixtures of these two. Acetic acid was also used. In mixed solvents

¹ Am. Chem. J., **28**, 329 (1902). Z. physik. Chem., **56**, 129 (1906).

² *Ibid.*, **30**, 193 (1903).

³ *Ibid.*, **32**, 521 (1904).

a minimum was found with the following salts: cadmium iodide, sodium iodide, and hydrochloric acid in mixtures of ethyl alcohol and water. That of cadmium iodide exists for dilutions up to 50 only, at 0°; beyond that there is no minimum. At 25° there is no minimum.

Somewhat surprising results were found with hydrochloric acid in methyl alcohol and water mixtures; μ_{∞} occurs at very low dilutions in mixtures containing up to 90 per cent. alcohol (between V_{100} and V_{200}), while in 100 per cent. methyl alcohol it is not found even as high as V_{2104} . In the dilutions above these limiting values there is a decrease in conductivity.

The relation pointed out by Wakeman,

$$\frac{\Delta}{p(100-p)} = \text{constant},$$

does not hold; neither does that of Cohen.

They explain the cause of the minimum as follows: There are two factors which determine conductivity, the amount of dissociation and ionic mobility. Decrease or increase of either of these produces a corresponding result in the conductivity.

They point out that there is a close connection between the fluidity and conductivity of a solution. These vary directly. When the solutions are brought together there is an increase in viscosity, or decrease in fluidity, which is its reciprocal. Consequently, the ions are much retarded in their movements and the conductivity diminished. As the temperature rises there is a shifting of the minima towards that mixture containing the greatest percentage of alcohol. In this shifting, however, the fluidity minima, they state, lag behind the conductivity minima.

They propose the following hypothesis: "The conductivities of comparable equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohol, other alcohols of the same series, acetone, etc.) are inversely proportional to the coefficients of viscosity of the solvent in question, and directly proportional to the association factor of the solvent

in question." These conclusions may be formulated as follows:

$$\frac{\mu_v}{x} = \text{constant, or } \frac{\mu_v \eta}{a} = \text{constant.}$$

The work of Jones and Bassett¹ with silver nitrate in both methyl alcohol-water and ethyl alcohol-water mixtures deals with the same phenomena as were previously discussed. There are well marked minima in the curves at both 0° and 25° in methyl alcohol-water mixtures, but no such minima occur in ethyl alcohol-water mixtures. In all cases, however, the curves fall much below the straight line of averages.

Jones and Bingham² measured the conductivities of lithium nitrate, potassium iodide, and calcium nitrate in water, methyl and ethyl alcohols and acetone, and binary mixtures of these solvents. They also made a large number of viscosity measurements of pure solvents, of mixed solvents, and of electrolytes in solution. In acetone and water mixtures the same minima which previous workers had observed were also observed. While the conductivity minima are intimately related to the minima of fluidity, the conductivity curves of different salts show marked differences. In acetone and alcohol mixtures the curves conform to the law of averages, that is, the conductivity curves are nearly straight lines. From this fact they conclude that the mixtures do not form more complex molecular aggregations.

A peculiar fact, and one not previously known, was here discovered. Lithium and calcium nitrates in mixtures of acetone with methyl or ethyl alcohol present a very pronounced maximum of conduction. This must be due to one of two causes: There is either an increase in dissociation and, consequently, an increase in the number of ions present, or there must be a diminution in the size of the ionic spheres, causing them to move more rapidly. We eliminate the first cause since fluidities of mixtures of acetone and the alcohols obey the rule of averages. This would indicate that there is no increase in the molecular aggregation in these mixtures, and

¹ Am. Chem. J., **32**, 409 (1904).

² *Ibid.*, **34**, 481 (1905).

according to Dutoit and Aston's hypothesis such a mixture would not dissociate to a greater extent than the constituent solvents. Since we can eliminate increased dissociation as the cause of the maximum, it must be due to the change in the dimensions of the ionic spheres. The previous work of Dutoit and Friederich and of Jones and Carroll is incomplete since it does not take into consideration the size of the ionic spheres.

The tendency to show maxima in conductivity increases from potassium iodide through calcium nitrate to lithium nitrate, which seem to show these effects most strongly. This may be connected with the ionic velocities, since potassium is a small ion and a comparatively rapidly moving one, and lithium forms, by combination with the solvent, a large ion and one that moves more slowly.

Jones and Rouiller¹ worked with silver nitrate in the solvents used by Jones and Bingham. In a general way they found results similar to those previously obtained. There is a striking similarity in the curves at 0° and 25° in mixtures of ethyl alcohol and acetone. There is a pronounced maximum at both 0° and 25° in the 25 per cent. acetone mixture in the more concentrated solutions, and shifting with increase in dilution through the 50 per cent. mixture to the 75 per cent. mixture. For pure acetone these curves decline rapidly. For mixtures of methyl and ethyl alcohols, the curves are nearly straight lines following the fluidity curves.

Jones and McMaster² worked with lithium bromide and cobalt chloride in the same solvents that had been employed by Bingham. The fluidities of water, methyl alcohol, ethyl alcohol, and acetone, and binary mixtures of these solvents were measured. The conductivities of these mixtures with water show a well-marked minimum. This minimum shows an intimate relation to that of fluidity. Lithium bromide in mixtures of methyl and ethyl alcohols gives no minimum in conductivity. The curves are nearly straight lines, except at the higher concentrations where there is a slight sagging

¹ Am. Chem. J., **36**, 42 (1906).

² *Ibid.*, **36**, 325 (1906).

at both temperatures. The same salt shows a maximum in conductivity in acetone-methyl alcohol mixtures with 75 per cent. acetone. The maxima increase with rise in temperature. In acetone-ethyl alcohol mixtures the same characteristics are manifested.

Cobalt chloride in methyl alcohol-water mixtures shows minima at both temperatures. At the higher temperature the minimum is most marked with 75 per cent. alcohol. In mixtures of ethyl alcohol and water, this salt shows a point of inflection at both temperatures and at all dilutions. These results are similar to those obtained by Jones and Bingham with calcium nitrate in acetone-water mixtures. In ethyl alcohol-methyl alcohol mixtures there is no distinct minimum but a sagging of the curve.

The minimum of fluidity corresponds to that of conductivity. There is in both methyl alcohol-water and ethyl alcohol-water mixtures a tendency of the minimum to shift towards the mixture containing the greatest percentage of alcohol whenever there is a rise in temperature. The authors reach the conclusion suggested by former workers that a diminution in the fluidity of the solvent, which would bring about a corresponding decrease in ionic mobility, is an important factor in causing the minimum in conductivity; and that the change in the size of the ionic spheres or the atmosphere which surrounds the ions should also be taken into account.

Several points in connection with the temperature coefficients are important. In nearly every case the temperature coefficients are smaller in the more concentrated solutions. Jones had already explained the phenomena in the following manner: In practically all solutions there is combination between solvent and solute. As dilution increases the solvates become more complex. Change in temperature affects most greatly the complex solvates, therefore we should expect the largest temperature coefficients at high dilutions.

At certain concentrations in methyl alcohol and acetone a negative temperature coefficient manifests itself. Conductivity varies directly as dissociation and fluidity. Since rise

in temperature diminishes dissociation, and increases fluidity, it would seem that there would be a point where these two influences would equalize each other, and the temperature coefficient become zero. This concentration is reached at V 200 in a 75 per cent. acetone and methyl alcohol mixture. Beyond this dilution there is a negative temperature coefficient.

Jones and Veazey¹ measured the conductivities and viscosities of solutions of copper chloride and potassium sulphocyanate in water, methyl alcohol, ethyl alcohol and acetone, and binary mixtures of these solvents. The minimum which was previously observed with different electrolytes is here also observed in some cases. This minimum is more pronounced at the higher dilutions. Where no minimum occurs there is a decided fall below the average value for the pure solvents. There is an interesting difference in the values for molecular conductivity in the pure solvent with increasing dilutions. In pure water, copper chloride, a ternary electrolyte, shows a much greater conductivity than potassium sulphocyanate, a binary electrolyte. In pure methyl alcohol the opposite condition exists. The conductivity of potassium sulphocyanate is the greater. This fact appears in previous work. Ethyl alcohol shows the same phenomenon.

The temperature coefficients of conductivity increase with increase in dilution. There is one exception—cobalt chloride in methyl alcohol. A marked negative temperature coefficient of viscosity is shown by potassium sulphocyanate in aqueous solutions.

In a recent communication Jones and Veazey² report the results of a study of solutions of tetraethylammonium iodide in mixtures of water, the alcohols and nitrobenzene. In mixtures of the alcohols and water there is a well-defined minimum in conductivity. In mixtures of the alcohols with each other there is no minimum, although the curves fall below the averages. In methyl alcohol and nitrobenzene the same phenomena occur, but in ethyl alcohol and nitrobenzene there is

¹ Am. Chem. J., **37**, 405 (1907). Z. physik. Chem., **61**, 41 (1908).

² Am. Chem. J., **41**, 433 (1909).

a maximum. The conductivity curves correspond very well with the fluidity curves.

Jones and Mahin¹ took up the study of cadmium iodide and lithium nitrate in binary mixtures of water, methyl and ethyl alcohols and acetone, and lithium nitrate in ternary mixtures of these solvents. Viscosity measurements of these solutions were also made. These measurements were carried to as high dilutions as possible—in some cases as high as 200,000 liters. At these high dilutions it was impossible to prevent considerable error due to the large correction for the specific conductivities of the solvents, and the large cell constants. With lithium nitrate the product of viscosity and molecular conductivity is nearly a constant for mixtures of acetone with methyl alcohol and ethyl alcohol. This value is independent of the temperature. The value is nearly 0.70, which is Walden's value for tetraethylammonium iodide. With acetone-water mixtures the product varies between 1.00, the value for water, and 0.63, the value for acetone.

Interesting results were obtained by determining the molecular weights of lithium nitrate in acetone by the boiling-point method. The object was to test the assumption that the low conductivity of this salt in ordinary solutions is due to the association of the salt. In the most dilute solution—0.09 normal—which could be determined accurately, the boiling-point method showed a molecular weight of 83.1, while the normal molecular weight is 69.07. We can, therefore, conclude that there is association, and this would account for the low conductivity in solutions at great dilutions.

Jones had already shown that cadmium iodide in acetone is associated. This salt was next investigated and found to behave like lithium nitrate in its molecular conductivity. There is an irregularity in the product of conductivity and viscosity in acetone and methyl alcohol mixtures, while in the pure solvents these products are nearly the same. In acetone-ethyl alcohol mixtures there is a fair degree of constancy in these products. Jones has shown that there is considerable polymerization of cadmium iodide in acetone.

¹ Z. physik. Chem., **62**, 41 (1908).

Conductivity and viscosity in ternary mixtures of the above solvents were next taken up, and a considerable amount of work was done. The object was to determine whether any essentially new principles could be discovered by increasing the number of components in the solvent mixture. The results are about what we would expect from a knowledge of the behavior of solutions in binary solvent mixtures.

Turner,¹ working in Jones's laboratory, made various conductivity measurements of potassium iodide, lithium chloride and lithium bromide in pure ethyl alcohol, at high dilutions. Many precautions were pointed out which were very helpful in the present work. The purification of solvents, precautions necessary to prevent contact with foreign substances, and other sources of error were investigated and discussed in detail. After repeated experiments it was found that small traces (0.2 to 0.3 per cent.) of water do not appreciably affect the conductivity.

The conductivity of potassium iodide in ethyl alcohol was measured up to a dilution of 450,000 liters. A maximum of molecular conductivity of 48.5 was reached at about 20,000 liters. From this the ionization was calculated. Measurements of conductivity were made at as high as 78°. The temperature coefficients increase with increasing temperatures and with increasing dilution. Ionization decreases considerably with rise in temperature. A 0.1 normal solution is dissociated 49 per cent. at 0°, 46 per cent. at 25° and about 35 per cent. at the boiling point of ethyl alcohol.

Determinations of ionization were also made by the boiling-point method, but these are in all cases considerably lower than those obtained by the conductivity method.

The work of Jones and Schmidt² introduces a new solvent, *glycerol*. They measured the conductivity and viscosity of lithium bromide, cobalt chloride, and potassium iodide in glycerol, methyl and ethyl alcohols, and binary mixtures of these and water. Glycerol was employed as a solvent because of its high viscosity. Its dielectric constant is about

¹ Am. Chem. J., **40**, 558 (1908).

² *Ibid.*, **42**, 37 (1909).

one-fifth that of water and it ought to have a fairly high dissociating power. It has remarkable solvent properties. But little work had previously been done with glycerol as a solvent. For measuring viscosity a viscometer with especially large bore had to be constructed.

Measurements of conductivity were made at 25°, 35° and 45°. Lithium bromide in mixtures of glycerol with water, methyl alcohol, and ethyl alcohol shows no minimum, but there is a wide departure from the law of averages, and a marked sagging in the curves. We would hardly expect a minimum since there is probably no mixture of glycerol with these other solvents which is more viscous than glycerol itself.

With cobalt chloride the conductivities in pure glycerol increase regularly. The conductivity values are considerably higher than the corresponding values for lithium bromide. Since cobalt chloride is a ternary electrolyte and lithium bromide a binary one, these results are just what we should expect. In pure ethyl alcohol, however, the case is different. The values for the conductivity of cobalt chloride are abnormally low. Lithium bromide, for instance, in a 0.1 N solution has a molecular conductivity of 15.8 at 25°. We should expect that cobalt chloride, since it is a ternary electrolyte, would have a conductivity probably 50 per cent. greater, but the value for the molecular conductivity of cobalt chloride in ethyl alcohol at the above concentration is only 4.71. Many of the halides of the heavy metals tend to form complexes when dissolved in organic solvents. It was supposed that the low conductivity of cobalt chloride in ethyl alcohol, at least in the more concentrated solutions, was due to polymerization of the molecules. Molecular weight determinations of cobalt chloride in ethyl alcohol were made by the boiling-point method. The mean of three determinations is 140 at about one-twelfth normal concentration, while the molecular weight for the compound CoCl_2 is 129.9. This would seem to indicate that there is association and, consequently, a lower conductivity than would be expected.

Potassium iodide in glycerol behaves like the other salts. There is a slight increase in conductivity with dilution. In

each case the conductivities for mixed solvents are less than the average for pure solvents.

A new feature is the magnitude of the temperature coefficients of conductivity. Some are almost as high as nine per cent. Cobalt chloride in ethyl alcohol manifests a negative temperature coefficient. A negative viscosity manifests itself in the case of potassium iodide in water, and in 25 per cent. and 50 per cent. glycerol and water at both 25° and 35° .

An elaborate investigation has been carried out in this laboratory during the past year by Guy on glycerol as a solvent. The results of this work will soon be published.

EXPERIMENTAL.

This investigation was undertaken for the purpose of obtaining facts by means of which the following questions might be answered:

1. At what dilutions do the maxima in conductivity occur for various salts in methyl and ethyl alcohols?
2. Is there any relation between these maxima in conductivity for different salts in different solvents?
3. What is the magnitude of the dissociation of these salts in these solvents as calculated by means of the maxima in conductivity?
4. What relation does this dissociation bear to that found by means of the boiling-point method?

Apparatus.

The Kohlrausch method was used. The wire was calibrated and was found to be of uniform thickness throughout.

The cells were of the latest type used in this laboratory. They were devised for measuring the conductivity of very dilute solutions where there is great resistance. They consist of two concentric platinum cylinders so placed one within the other that the electrodes are only about 1 mm. apart. They are held together by means of small drops of fusion glass placed between them. These electrodes have a surface of about 48.75 square cm. One of these cells had a constant as low as 2.82. The vertical position of the electrodes per-

mitted the ready escape of all air bubbles, neither were they difficult to wash and dry if the proper precautions were observed. These cells gave excellent results, and a sharp minimum was obtained upon the bridge without difficulty. The constants were determined by means of 0.01 N and 0.001 N solutions of potassium chloride. These constants were frequently redetermined but were found to change but little throughout the work.

All the apparatus was carefully calibrated. The necessary precautions concerning temperature were observed. The temperature in the 25° bath was regulated with a sensitive

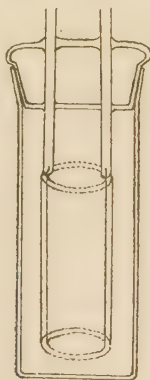


Fig. I.—Type of cell employed in this work.

thermometer calibrated against a German Reichanstalt thermometer. The 0° bath was from time to time tested to see that there was no change in temperature. At no time were measurements made when the temperature varied more than 0°.04 from that required. Careful tests were made to find the time required for the temperature of the solutions within the cells, both at 0° and 25°, to reach an equilibrium. This equilibrium was indicated by a constant conductivity. In all cases nearly an hour was necessary. Three readings were always taken and the mean was employed.

For 0° measurements a battery jar filled with ice and water was placed within a bucket and surrounded with ice and water. The cells were placed in the battery jar and covered

with glass. Ample time was allowed for the temperature to reach an equilibrium. Frequently the first reading was repeated after an interval of fifteen minutes or more, insuring equilibrium.

Extreme precautions were necessary in washing the apparatus. No fumes were permitted in the room. Immediately before using, the cells and flasks were thoroughly washed with distilled water, then rinsed several times with conductivity water and finally washed repeatedly with alcohol. This alcohol was always kept pure and used only a few times before it was dried and redistilled. Ether was not employed in drying since there is danger of fats being contained in it. The apparatus was then carefully dried. Before a solution was made up in a flask the latter was rinsed with a portion of the solvent, and the cell was rinsed with a portion of the solution. In many cases of very dilute solutions the flask in which the solution was to be made up was first cleaned, dried and rinsed with alcohol, the conductivity of this alcohol determined, and this same alcohol was employed to dilute the solution and its conductivity was used for the correction for the specific conductivity of the solvent. As a rule, there was little change in this conductivity when the above precautions were observed, and yet, because of the large volume, this change was at times quite appreciable.

Salts.

The salts used were potassium iodide, ammonium bromide, potassium sulphocyanate, lithium nitrate, sodium iodide, copper chloride, calcium nitrate and cobalt chloride.

In all cases the necessary precautions were observed in purifying the salts, Kahlbaum's best products being employed. All were recrystallized a number of times, finally from conductivity water and some from absolute alcohol. All were dried at a temperature of 125° – 150° . Those which are very deliquescent were heated for a long time, some for several days, in an air bath. Those chlorides which readily form oxychlorides when heated in the air were recrystallized several times, then dried in a vacuum desiccator over sulphuric acid

for several days, and finally heated for a long time in a current of dry hydrochloric acid gas. They were then placed in a desiccator over sulphuric acid and potassium hydroxide for several days. All other salts but the latter class were dried to constant weight before making up each solution.

Solvents.

The solvents used were methyl and ethyl alcohols and mixtures of these with water. Considerable difficulty was experienced in purifying methyl alcohol so as to obtain it with as low a specific conductivity as possible. This low conductivity was important since there was danger of introducing considerable error due to the large correction for the specific conductivity of the solvent at these high dilutions. It was evident from the results that some foreign substance was contained in the methyl alcohol which it was difficult to remove. It was supposed that this unusually high conductivity was due probably to pyridine bases, and that these might be removed by treatment with sulphuric acid. The cold alcohol was treated with a small quantity of dilute sulphuric acid. It was then distilled, the first runnings being always discarded, and the receiver removed while a considerable quantity was still in the flask. The alcohol was then boiled with lime for a day and distilled. In some cases it was repeatedly treated with lime and repeatedly distilled. One quantity thus treated gave a conductivity as low as 7.1×10^{-7} . On standing, however, the conductivity changed somewhat, so that not all work was done with alcohol having quite such low conductivity.

The ethyl alcohol was distilled from lime several times, then repeatedly distilled until it had a conductivity of about 2.6×10^{-7} . The water was purified by the method of Jones and Mackay.

Solutions.

All solutions were made by direct weighing. In those cases where the solutions were to be very dilute and but a small quantity of the salt was needed, a 0.1 N solution was made as a mother solution. This was then diluted to a second mother

solution. From this the final dilutions were made directly. Only in a few cases was a final dilution made from any other but the first or the second mother solution.

All solutions were made up at 20°. Enough time was always allowed for the temperature to come to equilibrium. The solutions when once placed in the cells were not removed from them until after measurements were made for both temperatures. They were never left in the cells longer than necessary because of possible decomposition:

Table I.—Conductivity of Potassium Iodide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	69.05	96.18	0.01572
2048	70.62	99.22	0.01620
4096	71.48	101.14	0.01660
8192	72.13	102.4	0.01679
16384	74.5	104.8	0.01627
32768	76.6	107.2	0.01598

Table II.—Conductivity of Potassium Iodide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	23.4	36.4	0.02222
2048	28.6	44.9	0.02280
4096	29.4	47.2	0.02422
8192	32.7	47.5	0.01810
16584	32.5	47.4	0.01834
33168	32.0	47.2	0.01900

Table III.—Conductivity of Ammonium Bromide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	66.1	93.1	0.01634
2048	69.9	94.1	0.01377
4096	70.6	96.7	0.01482
8129	71.8	96.8	0.01393
16584	69.2	94.9	0.01485

Table IV.—Conductivity of Ammonium Bromide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	32.1	37.0	0.02047
4096	25.2	39.6	0.02285
16384	27.5	39.1	0.01687
65536	29.8	39.5	0.01302

Table V.—Conductivity of Potassium Sulphocyanate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	69.1	98.3	0.01690
3200	71.1	101.0	0.01682
12800	73.0	103.7	0.01682
25600	83.5	106.3	0.01092

Table VI.—Conductivity of Potassium Sulphocyanate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	28.2	43.8	0.02218
3200	28.6	45.7	0.02391
6400	29.2	46.67	0.02393
12800	29.23	45.4	0.02213
25600	28.57	43.64	0.02110

Table VII.—Conductivity of Lithium Nitrate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	58.83	83.24	0.01659
3200	59.89	85.98	0.01743
6400	61.46	89.29	0.01811
12800	59.69	91.35	0.02121
25600	60.36	93.61	0.02203

Table VIII.—Conductivity of Lithium Nitrate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	23.82	36.67	0.02157
3200	24.13	38.44	0.02372
6400	25.63	40.87	0.02378
12800	25.87	40.02	0.02187
25600	...	43.30	0.00000

Table IX.—Conductivity of Sodium Iodide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
512	60.32	87.67	0.01814
1024	64.15	90.91	0.01669
2048	63.65	91.93	0.01777
4096	63.34	91.06	0.02382
8192	65.90	93.40	0.01669
16384	63.1	91.8	0.01819

Table X.—Conductivity of Sodium Iodide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
512	24.41	38.06	0.02237
1024	25.12	39.66	0.02315
2048	25.89	40.92	0.02322
4096	26.89	41.84	0.02224
8192	26.06	42.86	0.02579
16384	26.79	42.02	0.02274
32768	28.83	43.22	0.01996

Table XI.—Conductivity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	83.53	106.04	0.01078
3200	93.50	120.58	0.01156
6400	105.46	138.46	0.01252
12800	112.52	151.73	0.01394
25600	119.44	164.6	0.01509
51200	124.58	175.0	0.01620

Table XII.—Conductivity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	17.19	24.48	0.01696
3200	19.11	29.52	0.02179
6400	21.45	34.16	0.02370
12800	24.22	39.23	0.02537
25600	27.61	45.67	0.02616
51200	31.92	51.62	0.02469

Table XIII.—Conductivity of Cobalt Chloride in Methyl Alcohol
at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	101.94	138.58	0.01438
3200	110.98	152.34	0.01878
6400	115.76	162.38	0.01612
12800	116.22	165.74	0.01704
25600	115.34	166.08	0.01760
51200	112.58	157.96	0.01614

Table XIV.—Conductivity of Cobalt Chloride in Ethyl Alcohol
at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	19.99	25.61	0.01125
3200	22.75	30.13	0.01298
6400	25.68	34.15	0.01319
12800	29.25	39.01	0.01335
25600	31.36	43.62	0.01564
51200	31.62	46.31	0.01858
102400	28.42	(52.26)	0.00000

Table XV.—Conductivity of Copper Chloride in Methyl Alco-
hol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	64.13	78.58	0.09013
3200	75.43	89.31	0.07361
6400	85.22	101.28	0.07538
12800	91.3	112.3	0.09201
25600	90.5	116.4	0.01145
51200	79.1	112.1	0.01669

Table XVI.—Conductivity of Copper Chloride in Ethyl Alco-
hol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	16.08	20.96	0.01214
3200	18.94	25.74	0.01436
6400	21.06	30.70	0.01831
12800	22.52	34.16	0.02067
25600	22.94	37.79	0.02589

Table XVII.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	45.03	90.44	0.04023
2048	44.26	91.60	0.04278
4096	45.60	92.80	0.04140
8192	45.56	92.40	0.04112
16384	48.60	96.0	0.04000
32768	51.99	100.7	0.04517

Table XVIII.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	35.77	72.24	0.04078
2048	36.07	73.37	0.04137
4096	37.49	74.64	0.03968
8192	38.04	76.20	0.04013
16384	40.18	79.9	0.03945
36768	46.86	93.1	0.03948

Table XIX.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	41.63	71.37	0.04952
2048	41.20	72.00	0.05064
4096	41.82	73.19	0.05247
8192	44.98	75.41	0.05475
16384	46.83	75.3	0.05339
32768	49.95	71.8	0.01910

Table XX.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	32.38	74.80	0.05241
2048	32.75	76.23	0.05311
4096	32.73	76.60	0.05361
8192	33.88	77.20	0.05115
16584	35.30	80.3	0.05138
33168	39.88	86.8	0.04702

Table XXI.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	20.04	52.12	0.06401
2048	20.92	52.83	0.06073
4096	21.28	53.20	0.06000
8192	21.34	54.09	0.06120
16384	20.94	55.23	0.06550
32768	23.10	59.16	0.06244

Table XXII.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	20.58	44.14	0.04579
2048	21.39	45.04	0.04423
4096	21.50	45.91	0.04541
8192	21.34	45.96	0.04615
16384	21.85	47.85	0.04760
32768	23.68	51.04	0.04491
65536	25.11	53.30	0.04491

Table XXIII.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	66.85	144.1	0.04620
3200	68.20	148.5	0.04831
6400	69.39	151.8	0.04749
12800	70.50	152.3	0.04641
25600	72.08	159.0	0.04823
51200	80.30	181.6	0.05046

Table XXIV.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	53.94	113.5	0.04417
3200	55.84	115.7	0.04287
6400	56.59	119.4	0.04440
12800	57.86	122.3	0.04456
25600	58.70	124.1	0.04457
51200	65.2	138.6	0.04503

Table XXV.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	56.23	101.5	0.03220
3200	63.32	115.4	0.03290
6400	64.22	118.1	0.03356
12800	66.48	120.7	0.03262
25600	66.2	122.3	0.03390
51200	69.0	124.9	0.03241

Table XXVI.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	47.92	119.7	0.05992
3200	49.08	123.6	0.06072
6400	50.80	127.4	0.06032
12800	50.73	129.7	0.06227
25600	51.83	135.0	0.06419
51200	57.74	154.4	0.06697
102400	60.20	170.5	0.07327

Table XXVII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	31.16	81.56	0.06469
3200	32.27	84.67	0.06495
6400	32.70	86.56	0.06588
12800	33.70	88.28	0.06479
25600	33.25	87.42	0.06517
51200	34.18	90.8	0.07743
102400	34.40	89.7	0.07609

Table XXVIII.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	31.0	67.1	0.04658
3200	32.4	70.5	0.04704
6400	33.1	73.4	0.04870
12800	33.7	74.6	0.04855
25600	34.4	74.8	0.04698
51200	34.0	72.4	0.04518

Table XXIX.—Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	87.9	45.0*	35.8	41.6*	69.1
2048	88.5	44.3	36.1	41.2	70.6*
4096	88.9	45.6	37.5	41.8	71.5
8192	89.2*	46.6	38.0*	45.0	72.1
16384	89.2	46.6	40.2	46.8	74.5
32768	89.2	52.0	46.9	49.9	76.6

Table XXX.—Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 25°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	135.6	90.4	72.2	71.4	96.2
2048	136.2	91.6	73.4	72.0	99.2
4096	136.7	92.8*	74.7	73.2	101.1
8192	136.9*	92.4	76.2	75.4*	102.4
16584	136.9	95.3	79.9	75.3	104.8
33168	136.9	100.7	93.1	71.8	107.2

Table XXXI.—Conductivity of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	87.9	32.4	20.0	20.6	23.4
2048	88.5	32.8*	20.9	21.4	28.6
4096	88.9	32.7	21.3*	21.5*	29.4
8192	89.2*	33.9	21.3	21.3	32.7*
16584	89.2	35.3	20.9	21.8	32.5
33168	89.2	39.9	23.1	23.7	32.0
65536				25.1	

Table XXXII.—Conductivity of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 25°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	135.6	74.1	52.1	44.1	36.4
2048	136.2	76.2	52.8	45.0	44.9
4096	136.7*	76.6	53.2	45.9	47.2
8192	136.9	77.2	54.1	46.0*	47.5
16584	136.9	80.3	55.2	47.9	47.4*
33168	136.9	86.8	59.2	51.0	47.2

Table XXXIII.—Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	66.9	53.9	56.2	101.9
3200	68.2	55.8	63.3	111.0
6400	69.4	56.6	64.2	115.8
12800	75.5*	57.9	66.5*	116.2*
25600	72.1	58.7	66.2	115.3
51200	80.3	65.2	69.0	112.6

Table XXXIV.—Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 25°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	144.1	113.5	101.5	138.58
3200	148.5	115.7	115.4	152.34
6400	151.8	119.4	118.1	162.38
12800	152.3	122.3	120.7	165.74
25600	159.0	124.1	122.3	166.1
51200	181.6	136.6	124.9	158.0

Table XXXV.—Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	47.92	31.16	31.0	19.99
3200	49.08	32.27	32.4	22.75
6400	50.80*	32.70	33.1	25.68
12800	50.73	33.70*	33.7	29.25
25600	51.83	33.25	34.4*	31.36
51200	57.74	34.18	34.0	31.62*
162400	60.20	34.40	...	28.42

Table XXXVI.—Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 25°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	119.7	81.56	67.1	25.61
3200	123.6	84.67	70.5	30.13
6400	127.4	86.56	73.4	34.15
12800	129.7	88.28	74.6	39.01
25600	135.0	87.42	74.8	43.62
51200	154.4	90.8	72.4	46.31

Table XXXVII.—Dissociation of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	98.4	100.0	94.2	100.0	97.8
2048	99.2	...	95.0	...	100.0
4096	100.0	...	98.7	...	...
8192	...	...	100.0	...	...

Table XXXVIII.—Dissociation of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	98.4	98.7	93.9	95.8	71.5
2048	99.2	100.0	98.1	99.5	87.4
4096	100.0	100.0	100.0	100.0	90.0
8192	...	...	...	...	100.0

Table XXXIX.—Dissociation of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	100.0	88.6	...	84.5	87.6
3200	...	90.3	...	95.1	95.5
6400	...	91.9	...	96.5	99.6
12800	...	100.0	...	100.0	100.0

Table XL.—Dissociation of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	100.0	94.2	92.5	93.0	63.2
3200	...	96.6	95.7	94.1	72.0
6400	...	100.0	97.0	96.2	81.2
12800	...	...	100.0	97.9	92.5
25600	...	...	...	100.0	92.2
51200	...	...	...	...	100.0

Table XLI.—*Maxima in Molecular Conductivity for Certain Salts in Pure Alcohols.*

	0°.	25°.
KI in methyl alcohol	(77.5)	(112.6)
KI in ethyl alcohol	32.7	47.5
NH ₄ Br in methyl alcohol	71.8	96.8
NH ₄ Br in ethyl alcohol	(30.3)	39.6
KCNS in methyl alcohol	(69.2)	(110.4)
KCNS in ethyl alcohol	29.2	46.7
LiNO ₃ in methyl alcohol	61.5	(96.7)
LiNO ₃ in ethyl alcohol	25.9	40.8
NaI in methyl alcohol	64.1	91.9
NaI in ethyl alcohol	27.0	42.8
CuCl ₂ in methyl alcohol	91.3	116.4
CuCl ₂ in ethyl alcohol	(25.7)	(32.7)
Ca(NO ₃) ₂ in methyl alcohol		
Ca(NO ₃) ₂ in ethyl alcohol		
CoCl ₂ in methyl alcohol	116.2	166.0
CoCl ₂ in ethyl alcohol	31.6	(46.7)

Boiling-Point Data.

Table XLII.—*Sodium Iodide in Methyl Alcohol.*

Solvent.	Salt.	Concen- tration.	Rise.	Molecular rise.	Dissocia- tion.
53.949	2.8131	0.03478	0.429	12.33	46.8
55.352	2.7357	0.03300	0.425	12.90	53.6
61.195	2.5597	0.02790	0.3556	12.74	51.8
52.842	2.1082	0.02661	0.347	13.04	55.2
57.480	2.2060	0.02560	0.318	12.42	47.8
55.686	1.7227	0.02108	0.263	12.50	48.8
54.510	1.8380	0.02268	0.298	13.14	56.4
59.798	1.8080	0.02005	0.251	12.52	49.0
55.546	1.1943	0.01421	0.178	12.52	49.0
53.215	0.9665	0.01211	0.155	12.80	52.4

Table XLIII.—*Sodium Iodide in Ethyl Alcohol.*

Solvent.	Salt.	Concen- tration.	Rise.	Molecular rise.	Dissocia- tion.
53.100	3.1715	0.03984	0.585	14.63	27.7
54.734	2.7683	0.03374	0.512	15.17	31.9
64.744	3.2084	0.03303	0.495	14.98	30.2
53.896	2.6133	0.03235	0.481	14.87	29.3
61.293	2.5117	0.02730	0.402	14.73	28.0
55.509	2.0431	0.02455	0.365	14.86	29.1
61.701	2.1323	0.02306	0.351	15.22	32.3
59.294	1.9686	0.02214	0.327	14.76	28.3
54.368	1.5300	0.01877	0.281	14.97	30.1
64.926	1.4171	0.01455	0.223	15.32	33.2

Table XLIV.—Calcium Nitrate in Methyl Alcohol.

Solvent.	Salt.	Concen- tration.	Rise.	Molecular rise.	Dissocia- tion.
56.762	1.4954	0.01685	0.160	9.969	9.5
64.823	1.2154	0.01142	0.107	9.366	8.6
52.567	0.9792	0.01135	0.106	9.340	6.8
63.825	1.2489	0.01131	0.110	9.725	7.9
62.275	0.7453	0.00729	0.073	10.009	9.3

Table XLV.—Calcium Nitrate in Ethyl Alcohol.

Solvent.	Salt.	Concen- tration.	Rise.	Molecular rise.	Dissocia- tion.
50.476	1.1004	0.01328	12.68	0.168	5.1
54.301	1.3570	0.01228	12.86	1.158	5.9
52.355	0.6795	0.00791	12.51	0.099	4.4

Table XLVI.—Cadmium Iodide in Ethyl Alcohol.

Solvent.	Salt.	Concen- tration.	Rise.	Molecular rise.	Dissocia- tion.
48.831	3.5915	0.02007	0.253	12.60	4.8
54.657	3.6962	0.01850	0.230	12.43	4.05
50.956	3.1632	0.01694	0.214	12.63	4.9
51.574	2.9277	0.01549	0.195	12.58	4.7
52.348	2.7683	0.01443	0.181	12.57	4.6
52.316	2.6784	0.01397	0.176	12.58	4.6
48.034	2.1137	0.01201	0.152	12.67	5.0
51.668	1.2491	0.00660	0.082	12.42	4.0
56.563	0.8712	0.04204	0.052	12.38	4.3

DISCUSSION OF RESULTS.

Tables I to XVI show the conductivity of the various salts worked with in the pure solvents at both 0° and 25°. Nine of these tables show a maximum either at one or both temperatures. The other tables show no maximum up to the highest dilutions measured. In several cases maxima occur at one temperature and none at the other. In some tables the maxima occur at the same concentration at both temperatures; in others at different concentrations, but they always occur at concentrations which are close together. The tem-

perature coefficients in general agree very well. Nearly all show a slight increase with increasing dilution.

Tables XVII to XXVIII show the conductivity of potassium iodide and cobalt chloride in mixtures of methyl alcohol and water at both 0° and 25° . In some of these tables the maximum conductivities are reached. The maxima generally occur at a greater concentration at 0° than at 25° . In a few tables the maxima occur at the same concentration at both temperatures. In nearly every case where there is a maximum there is a slight decrease in conductivity, then a rapid increase as dilution increases, thus giving an inflection in the curve.

Figs. II to IV give the curves for the conductivities of potas-

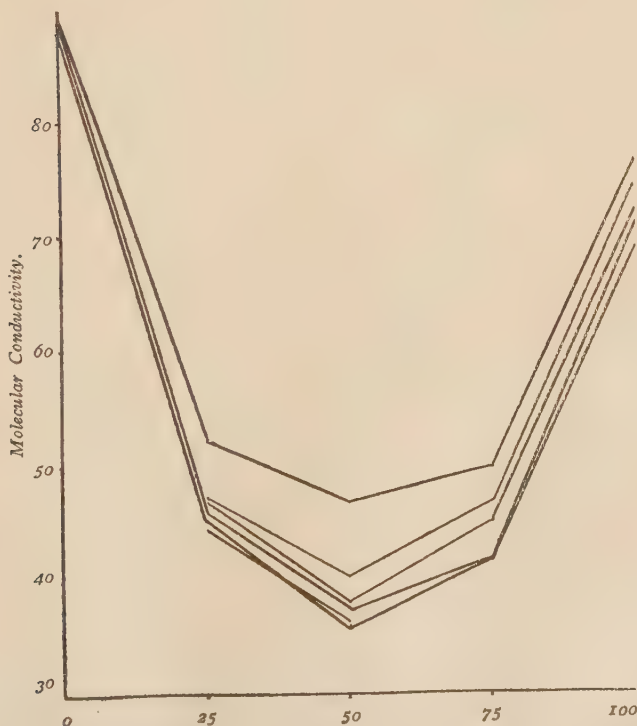


Fig. II.—Conductivity of potassium iodide in mixtures of methyl alcohol and water at 0° .

sium iodide in mixtures of methyl alcohol and water and of ethyl alcohol and water. The abscissas represent the percentage of alcohol and the ordinates represent the conductivity.



Fig. III.—Conductivity of potassium iodide in mixtures of methyl alcohol and water at 25°.

ity. In Fig. II there is a marked minimum with 50 per cent. methyl alcohol. Fig. III shows a minimum with 75 per cent. methyl alcohol. Fig. IV for potassium iodide in methyl alcohol-water mixtures shows the same characteristics. Fig.

V shows a minimum for only three concentrations; these are with 75 per cent. ethyl alcohol.

Figs. VI to IX are the curves for the conductivity of cobalt chloride in methyl alcohol-water mixtures and ethyl alcohol-water mixtures at both 0° and 25° . Fig. VI shows a minimum

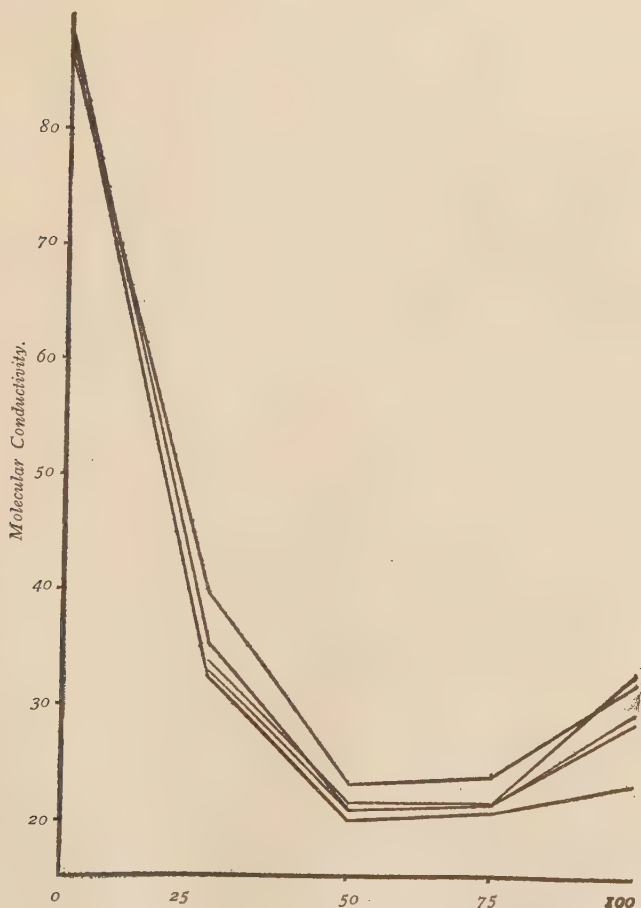


Fig. IV.—Conductivity of potassium iodide in mixtures of ethyl alcohol and water at 0° .

with 50 per cent. methyl alcohol. Fig. VII shows minima in the curves with 75 per cent. methyl alcohol. In Figs. VIII and IX there is no minimum.

Tables XIX to XXXVI represent the values for the conductivities of potassium iodide and cobalt chloride in mixed solvents, arranged according to temperature. The propor-



Fig. V.—Conductivity of potassium iodide in mixtures of ethyl alcohol and water at 25°.

tions in which the solvents are mixed and the concentrations vary. A study of the maxima of conductivity in these tables is interesting. The more probable values for μ_{∞} are indicated by a (*). By means of these values I have calculated the dis-

sociation of the salts at different volumes for four of these tables (XXIX, XXXI, XXXIII, and XXXV), since these present more μ_{∞} values than the rest. I have used the well-known equa-

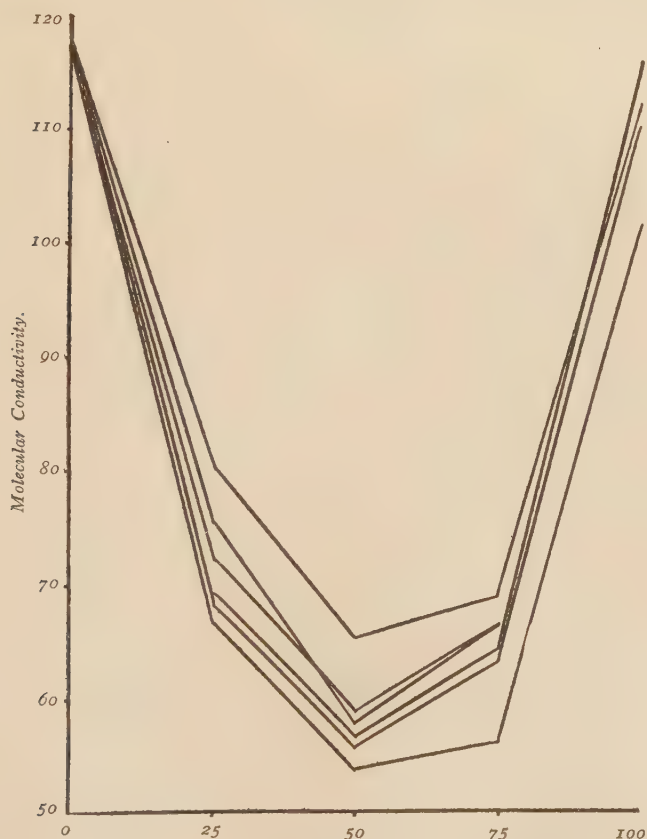


Fig. VI.—Conductivity of cobalt chloride in mixtures of methyl alcohol and water at 0°.

tion, $\alpha = \frac{\mu}{\mu_{\infty}}$ and the values for α are given in Tables XXXVII to XL. In Table XXXIII no μ_{∞} occurs for 50 per cent. methyl alcohol-water mixtures.

These values for dissociation are interesting when compared with the values for the corresponding molecular conduc-

tivities. Fig. X gives the curves for dissociation corresponding to the molecular conductivity as indicated by the curves in Fig. IV. Fig. XI in the same manner corresponds to Fig. VI and Fig. XII to Fig. VIII.

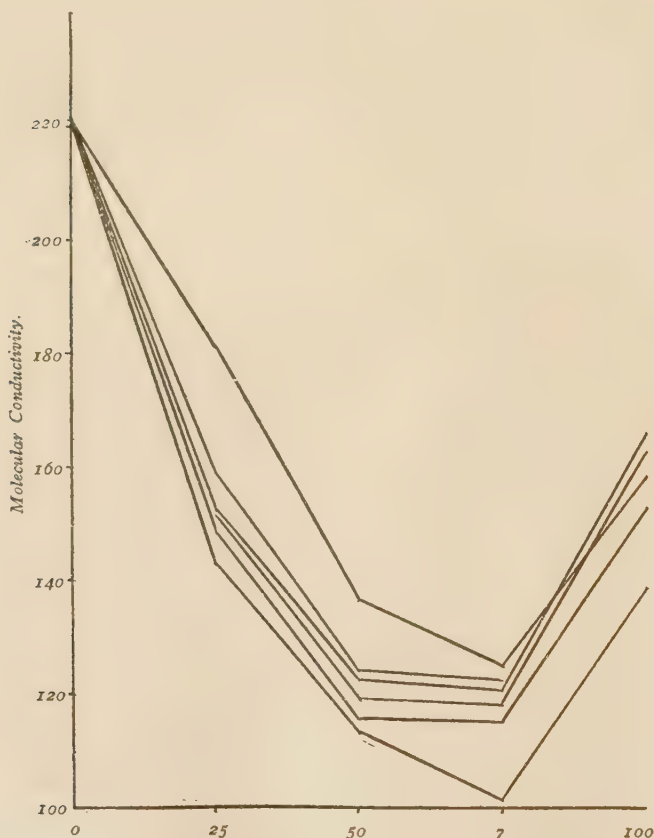


Fig. VII.—Conductivity of cobalt chloride in mixtures of methyl alcohol and water at 25°.

In Fig. IV the conductivity curves of potassium iodide in ethyl alcohol-water mixtures at 0° show minima for all dilutions, while the corresponding curves for dissociation in Fig. X at first rise. If the equation $\alpha = \frac{\mu_v}{\mu_\infty}$ holds for mixed sol-

vents this would indicate that at 0° the dissociation in 25 per cent. ethyl alcohol-water mixtures is slightly greater than in pure water. In all mixtures the dissociation is very much greater than it is in pure alcohol.

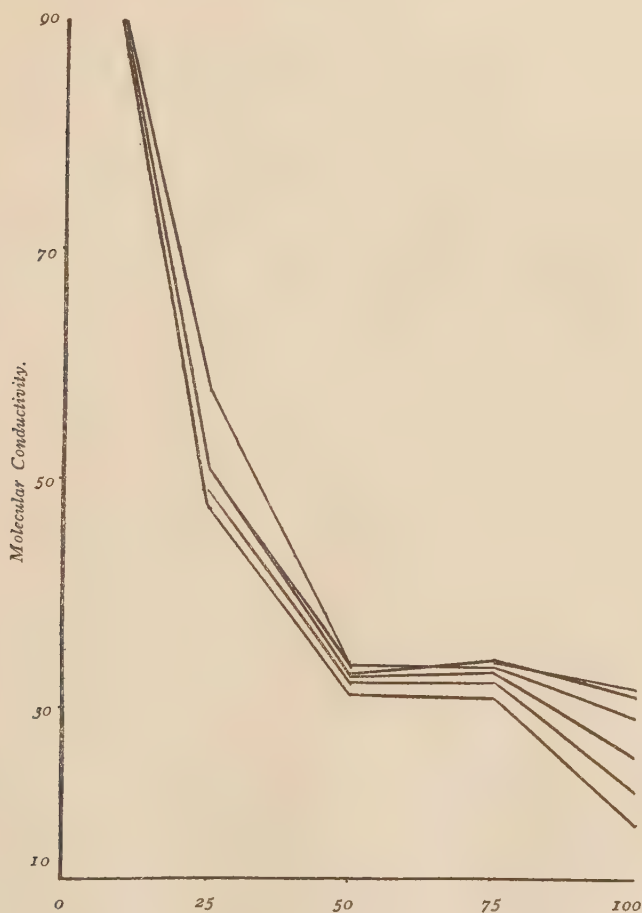


Fig. VIII.—Conductivity of cobalt chloride in mixtures of ethyl alcohol and water at 0° .

Fig. XI gives the curves for cobalt chloride in methyl alcohol-water mixtures corresponding to the molecular conductivity as represented by Fig. VI. The curves for dissocia-

tion show minima, but the drop below the straight line of averages is very small when compared with the large and decided minima in Fig. VI.

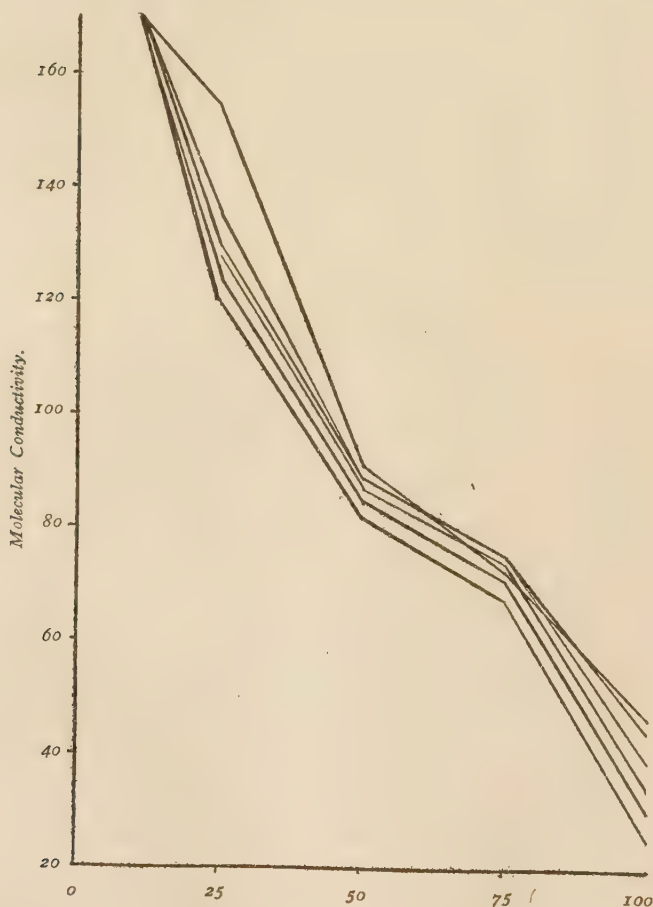


Fig. IX.—Conductivity of cobalt chloride in mixtures of ethyl alcohol and water at 25°.

Fig. XII for dissociation corresponds to Fig. VIII for molecular conductivity. The relation between these two figures is similar to the relation between X and IX. In both cases the mixed solvents are ethyl alcohol and water. In this case

we have a binary salt, and the curves for Figs. X and XII are strikingly similar.

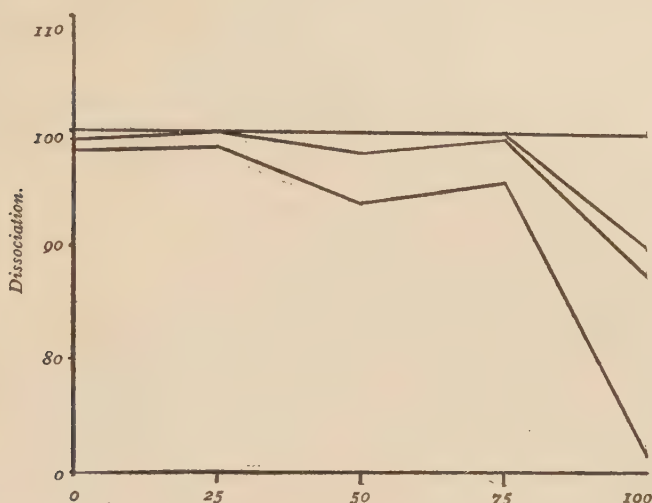


Fig. X.—Dissociation of potassium iodide in mixtures of ethyl alcohol and water at 0°.

The curves representing dissociation in ethyl alcohol-water mixtures are sometimes upward curves, taking a direction oppo-

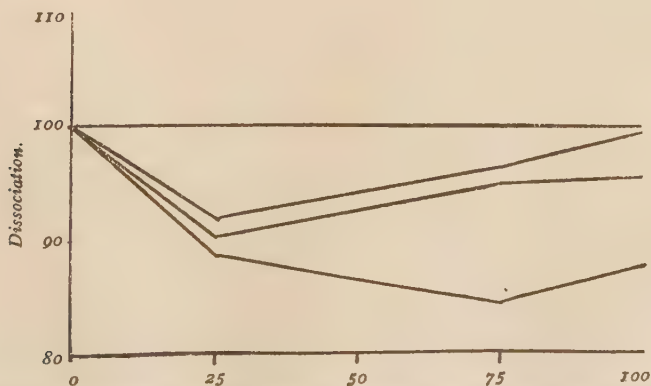


Fig. XI.—Dissociation of cobalt chloride in mixtures of methyl alcohol and water at 0°.

site to that of the curves representing conductivity, which are downward curves. This fact is especially apparent when Fig. IV,

giving the curves for the conductivity of potassium iodide in mixtures of ethyl alcohol and water at 0° , is compared with Fig. X, which gives the curves for the dissociation of these same solutions. This plainly indicates that the greatly diminished conductivity in mixed solvents is due not to diminished dissociation but to the other factor conditioning conductivity, *viz.*, diminished velocity of the ions through the solution. Though it had been previously pointed out that this diminished

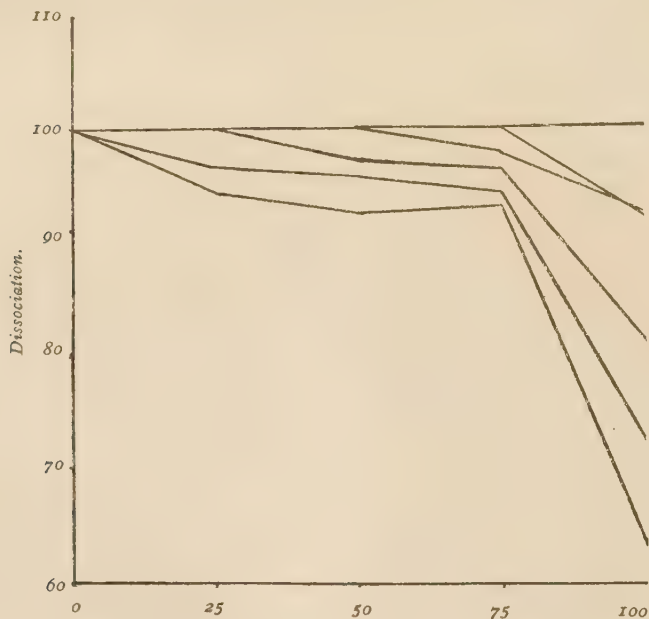


Fig. XII.—Dissociation of cobalt chloride in mixtures of ethyl alcohol and water at 0° .

conductivity is due almost entirely to increased viscosity of the mixed solvent, it was not definitely known what the magnitude of the dissociation in these mixed solvents is, nor was it suspected that this dissociation might be greater in the mixed than in the pure solvents, as is shown to be the case by the curves for dissociation, some of these curves having maxima while those of conductivity have decided minima. These facts are quite marked where ethyl alcohol-water mixtures are used

as solvents. In such cases the increased viscosity, on the one hand, diminishes the conductivity, and the decreased dissociation, on the other, increases the conductivity. The viscosity in this case, since it is the more potent factor, causes the large minima in the curves for conductivity. These minima would be more marked than they are were it not for the slightly increased dissociation.

Table XLI gives the μ_{∞} values of molecular conductivity for the various salts studied both in methyl and in ethyl alcohols at 0° and at 25° , whenever such values could be found. The values without the brackets were determined experimentally. Those within the brackets could not be determined experimentally because of the great dilutions and consequently unavoidable errors, but were calculated by a method given below.

An examination of the table reveals the fact that there is some relation between the maximum for each salt in the different solvents at any given temperature. It was suspected that this relation is a constant and that the following equation would hold:

$$\frac{\mu_{\infty} \text{ methyl}}{\mu_{\infty} \text{ ethyl}} = \text{constant.}$$

This equation was then applied with the following results:

Binary Electrolytes.

LiNO_3 at 0° = 2.37.

NaI 0° = 2.37.

NH_4Br 25° = 2.44.

NaI 25° = 2.17.

Ternary Electrolytes.

CoCl_2 at 0° = 3.68.

These facts make it appear probable that there is approximately such a constant for binary electrolytes and another for ternary electrolytes. These data are not sufficient, however, to give a final value to such constants. Further investigations will be required for this purpose. Most of these maxima occur

at dilutions of $V = 12,800$ to $V = 51,200$. At these dilutions it is very difficult to obtain accurate results and the values for the constant are probably within the limits of experimental error.

The value for the constant between methyl and ethyl alcohols for binary electrolytes appears to be very nearly 2.37. I have obtained but one value for ternary electrolytes, which is 3.68. That is nearly 1.5×2.37 . The latter value (3.56) is probably the more nearly correct. The factor 1.5 is employed since this expresses the ratio of ions present between binary and ternary electrolytes at complete dissociation.

With the data in hand I proceeded to test further the accuracy of the above equation by supplying by calculation in Table XLI those μ_{∞} values which could not be determined experimentally. The value of the constant was taken as 2.37 for binary electrolytes and 3.56 for ternary electrolytes. The calculated value for potassium iodide in methyl alcohol at 0° from the value in ethyl alcohol would be 77.5. An examination of Table I reveals the fact that this value is probably very nearly correct. For 25° it would be 112.6. Again from the same table this is probably correct. Ammonium bromide in ethyl alcohol at 0° would be equal to 30.3. This too as indicated by Table IV is probably nearly correct. Potassium sulphocyanate in methyl alcohol at 25° would have a value of 110.4. Table V indicates that this value is probably correct within the limits of experimental error. Lithium nitrate gives a value of 96.7 in methyl alcohol at 25° ; compared with Table VII this would seem to be nearly correct.

With ternary electrolytes there are only three cases to which this equation can be applied. Copper chloride in ethyl alcohol at 0° would give a value of 24.8, and cobalt chloride in ethyl alcohol at 25° would give 46.7 as the value for the maximum in conductivity. In Table XIV, at 0° , a maximum is reached at $V = 25600$. The maxima at the different temperatures as a rule do not occur very far apart. We believe that the value 46.7 is pretty nearly correct for the maximum for cobalt chloride in ethyl alcohol at 25° . The only two values which do not fit into the table are the value for potas-

sium cyanide in methyl alcohol at 0° and that for copper chloride in ethyl alcohol at 25° . The latter, however, is not far from what we might expect it to be.

I believe from the above results that the ratio between the maxima in molecular conductivity for different salts in methyl alcohol and the maxima for the same salts in ethyl alcohol is probably constant for all binary electrolytes, that for all ternary electrolytes it is a constant of different value, and that there is a definite relation between these two constants.

Jones, in an article on "The Electrolytic Dissociation of Certain Salts in Methyl and Ethyl Alcohols, as Measured by the Boiling-Point Method," gives the following table which expresses "the dissociation values of the above alcohols as calculated from data obtained by the boiling-point method." The ratios of these values were calculated and are also expressed in the table:

Table XLVII.

Substance.	Dilution normal.	Dissociation in methyl alcohol.	Dissociation in ethyl alcohol.	Ratio.
		Per cent.	Per cent.	
KI	0.1	52	25	2.08
NaI	0.1	60	33	1.8
NaBr	0.1	60	24	2.5
NH ₄ Br	0.2	49	21	2.3
CH ₃ COOK	0.1	36	16	2.3
CH ₃ COONa	0.1	38	14	2.7
Ca(NO ₃) ₂	0.1	15	5	3.0

Leaving out the value 1.8 for sodium iodide, which is evidently erroneous, we obtain as a mean from the other values of the binary electrolytes 2.37 which, it will be remembered, is the same as the value obtained above by the conductivity method for the ratio between the maxima in the different alcohols. The value in this table for the one ternary electrolyte is not so great as that determined by the conductivity method, and yet it is possible that more data would give comparable values.

The boiling-point data in this work were obtained by means

of the boiling-point apparatus used by Jones.¹ Both solvents were carefully purified and dried.

Table XLIV gives the dissociation of certain salts as calculated by both the conductivity and boiling-point methods:

Table XLIV.

Salt.	Solvent.	Dissociation from conductivity method. Per cent.	Dissociation from boiling-point method. Per cent.
KI	Methyl	65	49
KI	Ethyl	49	26
NaI	Methyl	75	61
NH ₄ Br	Methyl	71	47
NH ₄ Br	Ethyl	40	20

It will be seen at a glance from the above table that the dissociation values as determined by conductivity are higher than those found by the boiling-point method, in both methyl and ethyl alcohols. This may possibly be due to a polymerization of the undissociated molecules in the solvent in question. This would give too low dissociation as measured by the boiling-point method, since this method takes into account both the molecules and the ions, while the conductivity method deals only with the ions.

SUMMARY.

I have measured the conductivity of various salts in pure methyl and ethyl alcohols at very high dilutions, and also in mixtures of methyl and ethyl alcohols with water. In many of these measurements I have found the value of μ_{∞} .

Many of these values were found to occur at concentrations between $V = 3200$ and $V = 51200$.

A constant ratio was found between the values of μ_{∞} for several binary electrolytes in methyl alcohol and in ethyl alcohol, and the ratio for one ternary electrolyte was worked out. These facts indicate that there is a definite relation between these two ratios.

I have found minima in most of the curves for mixed solvents.

I have tabulated the dissociation of several salts in methyl alcohol and ethyl alcohol as determined by the boiling-point method.

¹ Z. physik. Chem., **31**, 114 (1899) (Jubelband zu van't Hoff)

BIOGRAPHY

The author of this dissertation, Henry Royer Kreider, was born near Millheim, Pennsylvania, April 24, 1874. His preparatory training was received in the public schools and in the Spring Mills Academy. He entered Franklin and Marshall College in 1894 from which he received the degree of A.B., in 1898, and A.M., in 1901. Since then he has taught in different schools and academies. The year 1904-5 was spent in graduate work at the Johns Hopkins University. After teaching for several years in the Pennsylvania State-Forest Academy he again entered the Johns Hopkins University in 1907. For several years since then a part of the time was devoted to teaching.

